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Beth Pearson-Naul

**APPLICATION FOR UNITED STATES LETTERS PATENT**

**FOR**

**METHOD FOR IMPROVED PRODUCTION OF CYCLOHEXENYL  
AND ALKENYL AROMATIC COMPOUNDS**

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# METHOD FOR IMPROVED PRODUCTION OF CYCLOHEXENYL AND ALKENYL AROMATIC COMPOUNDS

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## **BACKGROUND OF THE INVENTION**

### **1. Field of the Invention**

[0001] This invention relates to the preparation of cyclohexenyl and alkenyl aromatic compounds. In particular, the invention relates to the preparation of  
10 styrene.

### **2. Background of the Art**

[0002] Among the cyclohexenyl and alkenyl aromatic compounds finding the  
15 most extensive use around the world is styrene. Styrene is utilized widely in the plastics industry for the manufacture of plastics, rubber-modified impact polystyrene, acrylonitrile-butadiene-styrene terpolymer, styrene acrylonitrile copolymer, styrene-butadiene type synthetic rubber, and a host of other copolymers, terpolymers, and the like. While a wide variety of methods of  
20 producing styrene are now known, one of the simplest and most economical methods involves using a benzene feed which is converted, via alkylation, to ethylbenzene and then, via continuous dehydrogenation, to a process stream comprising styrene, toluene and benzene products. The dehydrogenation may be done catalytically in an adiabatic or isothermal reactor. Primary products are  
25 styrene, unreacted ethylbenzene, and smaller amounts of toluene and benzene. The process stream components are then separated via a distillation columns, with the styrene and toluene being recovered as products, and the benzene being recycled to begin the alkylation phase again.

[0003] A problem that is encountered during this process is that additives such  
30 as amines for neutralization of carbonic acid in process water and inhibitors to

decrease styrene polymerization are added. Common stabilizers and neutralizers include amine compounds, which effectively inhibit the styrene homopolymerization and neutralize the carbonic acid but unfortunately byproducts are then retained with the benzene fraction. Such nitrogen compounds are undesirable in the benzene fraction because they tend to interfere with the alkylation and/or hydrogenation catalysts when the benzene is recycled in the process. Generally the nitrogen compounds therefore require an additional filtration step of the benzene through a clay or zeolitic bed to absorb them. This bed must be appropriately maintained to ensure continued efficacy in removing the nitrogen compounds.

### **SUMMARY OF THE INVENTION**

[0004] In one aspect, the present invention is a process for preparing cyclohexenyl or alkenyl aromatic compounds. The process includes alkylation of a cyclohexane or aromatic compound; dehydrogenation of the alkylated cyclohexane or aromatic compound to form a process stream including a cyclohexenyl or alkenyl aromatic compound; and separating the process stream into a cyclohexenyl or alkenyl aromatic compound rich fraction and a cyclohexane or aromatic compound rich fraction. The process also includes adding nitrogen-containing compounds at one point in the process and using water to extract the nitrogen-containing compounds, or the break down products of the nitrogen-containing compounds, from the cyclohexane or aromatic compound rich fraction at another point in the process.

[0005] In another aspect, the present invention is a process for preparing styrene. The process includes alkylating benzene to form ethylbenzene, dehydrogenating ethylbenzene to form a process stream containing styrene, unreacted ethylbenzene, benzene and toluene products, separating the process

streams into styrene, benzene and toluene fractions, and recycling the benzene fraction back into the process. The process also includes adding a nitrogen-containing compound at one point in the process and using water to extract the nitrogen-containing compounds, or the break down products of the nitrogen-containing compounds, from the benzene fraction at another point in the process.

[0006] In still another aspect, the present invention is, in a process for preparing cyclohexenyl or alkenyl aromatic compounds, wherein the process includes an alkylation of a cyclohexane or aromatic compound; a dehydrogenation of the alkylated cyclohexane or aromatic compound to form a process stream; and a separation of the process stream into a cyclohexenyl or alkenyl aromatic compound rich component and a cyclohexane or aromatic compound rich component; and the process also includes the use of nitrogen-containing compounds, an improvement of using water to extract the nitrogen-containing compounds from the cyclohexane or aromatic compound rich component.

### **DETAILED DESCRIPTION OF THE EMBODIMENTS**

[0007] The present invention is useful in a process for preparing cyclohexenyl and alkenyl aromatic compounds, such as styrene, that include alkylation of benzene to form ethylbenzene, followed by dehydrogenation of ethylbenzene to form a process stream containing styrene, benzene and toluene products, which are then separated into styrene, unreacted ethylbenzene, benzene and toluene fractions, and the benzene fraction is recycled. Nitrogen compounds are employed to prevent homopolymerization of the styrene product. Amine compounds are also injected into the process to neutralize carbonic acid in the water phase of the process. In this process the invention provides an improvement comprising intimately contacting the benzene fraction with water

and then removing the water containing nitrogen compounds from the benzene fraction prior to alkylation of the recycled benzene fraction.

[0008] The present invention thus includes many possible embodiments, since the water can be injected at more than one possible point during the process, and can likewise be removed at more than one point, and via more than one means. In one embodiment, the water is injected with the fresh benzene prior to alkylation, which is also prior to the entry of the recycled benzene; the fresh and recycled benzenes are thoroughly mixed; and then they are passed through a drying column which removes the water and the entrained nitrogen compounds and passes the now-dry benzene on to the alkylation unit.

[0009] In accordance with the present invention, styrene is continuously mass produced in a dehydrogenation process of ethylbenzene in any type of reactor conventionally employed for a continuous mass styrene production process. For example, a reactor is charged with ethylbenzene under dehydrogenation conditions and a styrene-, unreacted ethylbenzene-, benzene- and toluene-containing process stream is formed. Neutralizing amines such as morpholine as added to the stream to increase the pH of the co-existing water phase. Stabilizing compounds that contain nitrogen, such as 2,6-dinitro-p-cresol, 4-tert-butylcatechol, 7-substituted quinone methides, phenyldiamine, 2,6-dinitro-p-cresol, N,N-bis(hydroxypropyl)hydroxylamine, and other amine compounds, may then be added to the organic phase of the process stream to prevent homopolymerization of the styrene and then the process stream passes to a separation unit where the three products are separated into fractions and removed, with the stabilizing compounds retained primarily with the tar fraction.

[0010] The benzene fraction can include nitrogen compounds and/or their breakdown products. It can therefore be desirable to treat the benzene fraction in some way to remove the nitrogen compounds prior to recycling the benzene

fraction back into the process. Such treatment may include passing through an absorbent bed that includes as the absorbent material at least one adsorbent such as a zeolite, activated carbon, clay, alumina, and the like. Other possible treatments include further distillation, fractionation, or additional separation steps. Following removal of the nitrogen compounds, the benzene fraction is ready for recycle to the alkylation phase of the process, where it is to be first mixed with fresh benzene or added directly to the process as a separate stream. [0011] The method of the present invention finds particular use in commercial systems where economics represent a driving factor. It has been found that when the benzene containing the nitrogen compounds is intimately mixed with water, the major portion of the nitrogen compounds preferentially entrain with the water, and therefore can be easily removed simply by removing the water. Thus, the need for use of an absorbent bed is greatly minimized, thus reducing maintenance and replacement requirements, and addition of water is a relatively negligible cost. This combination makes application of the present invention highly desirable in commercial styrene production at most of the world's styrene production facilities.

[0012] In applications of the present invention it can be desirable to ensure that the contact between the nitrogen-containing benzene fraction and the water is sufficiently intimate to maximize the entrainment of the nitrogen compounds. Thus, a relatively high degree of mixing is strongly preferred. This mixing can take place at more than one point in the production process, thus presenting a process improvement that can be adapted to some extent to fit the configuration of the apparatuses being employed.

[0013] For example, in one embodiment water can be injected at a point in the process that is shortly after the separation of the dehydrogenation product fractions, styrene, toluene and benzene in the case of styrene production. With

appropriate injection and flow line design, as will be obvious to those skilled in the art, the water will achieve an intimate mixing with the benzene fraction. The water, containing the now-entrained nitrogen compounds, is then removed via, for example, use of a simple separation unit designed to remove water based upon differentiation of density; a distillation unit; conventional stripping or other drying means; and the like. The "cleaned" benzene can then be routed to the alkylation unit where it can be, optionally, mixed with fresh benzene, and then converted into more ethylbenzene.

[0014] In another embodiment, the nitrogen-containing benzene that has been separated from the styrene and toluene is refluxed directly for mixing with the fresh benzene, and water is added at the same point. Again, assuming appropriate flow design to ensure intimate mixing of all components, the nitrogen compounds quickly and preferentially transport into the water phase. At this point the benzene/water process stream can be passed through a distillation unit, drying column, fixed adsorbent bed, or other means to remove the water and, therefore, the nitrogen compounds.

[0015] The proportion of water can be important in some embodiments of the present invention, particularly where the levels of nitrogen compounds are comparatively high. Desirably the water is employed in an amount that is sufficient to optimize entrainment of the undesirable nitrogen compounds, but not of such an excess that removal of the water becomes unnecessarily problematic. In one embodiment a proportion of water ranging from about 1 percent to about 10 percent, based on weight of benzene, is employed, which is equivalent to from about 10,000 ppm water to about 30,000 ppm of water in benzene. In another embodiment the proportion of water ranges from about 2 percent to about 4 percent, based on weight of benzene. Most consistent performance is generally found when the water is deionized water, boiler feed

water, or steam condensate which reduces potentially adverse side reactions accruing from the presence of even very low amounts of conventional water treatment compounds.

5 [0016] It is also desirable to ensure that contact of the water with the nitrogen-containing benzene is of sufficient duration to optimize removal of the nitrogen compounds without interfering with the flow of the continuous process. Thus, design of the benzene reflux and water-injection systems should take the flow rates into account and should be designed to optimize this time. In one embodiment the intimate contact is maintained for at least about 1 minute. In  
10 another embodiment the intimate contact is maintained for at least about 5 minutes. Generally, longer times promote increased nitrogen compound removal, with the goal being to remove at least about 90 percent of such compounds.

15 [0017] Ultimately it is desirable to remove the water via the selected drying means such that no more than about 900 ppm water remains, which is sufficient in many cases to enable recycle of the benzene. However, the present industry standard demands that no more than about 50 ppm remain for optimum performance, and this level should be easily attainable using any of the conventional drying technologies mentioned hereinabove.

20 [0018] The benefits of the present invention include, in particular, the need for less frequent regeneration of the alkylation catalyst or catalysts, and also less frequent change-out of the absorbent beds currently used to remove most of the nitrogen compounds from the benzene fraction prior to recycle. While it may still be desirable to employ such beds with the present invention, they will thus  
25 require significantly less maintenance, and the amount of nitrogen compounds that do ultimately reach the alkylation catalyst in the recycled benzene will be



greatly minimized in comparison with recycled benzene which has not been subjected to the practice of the present invention.

### **EXAMPLE**

- 5 The following example is provided to illustrate the present invention. It is not, however, intended to be, nor should it be construed, as being limitative of the scope of the invention in any way.

#### Example 1

- 10 The equilibrium concentration of nitrogen compounds in water in contact with a benzene fraction that has been separated from a stabilized styrene-, benzene-, and toluene-containing process stream is determined using a gas chromatography method utilizing the ANTEK 7090 SCD/NCLD with automated gas and/or liquid sampling valves. The ANTEK 7090 SCD/NCLD is available from ANTEK Instruments L.P. The equilibrium concentration is determined to be  
15 18.0 ppm.

- Water is injected at two different rates, 0.1 gal/min [0.3785 l/min] and 0.2 gal/min [0.7516 l/min], into a flow line containing the benzene fraction process stream and then recovered and analyzed using the same method of above. The nitrogen concentration of the sample taking during the 0.1 gal/min water injection  
20 is 17.0 ppm. The nitrogen concentration of the sample taking during the 0.2 gal/min water injection is 19.0 ppm.

- These observations can be interpreted to mean that the distribution of nitrogen compounds in the water phase is at equilibrium for the distribution of these compounds between the oil and water phases. A higher rate of water injection  
25 with equal or greater concentration of nitrogen compounds shows that the water injection is removing nitrogen compound from the oil phase.

It is further noted that while a part of the foregoing disclosure is directed to some embodiments of the invention, various modifications will be apparent to and appreciated by those skilled in the art. It is intended that all such variations within the scope of the claims and are embraced by the foregoing disclosure.